

**COMMENT ON “OSCILLATORY INDIRECT INTERACTION BETWEEN
ADSORBED ATOMS – NON-ASYMPTOTIC BEHAVIOR IN TIGHT-BINDING
MODELS AT REALISTIC PARAMETERS” BY K.H. LAU AND W. KOHN**

Received 28 December 1977

Earlier in this issue, Lau and Kohn [1] (hereafter LK) have carefully calculated the asymptotic form of the indirect electronic [“pair”] interaction between two adatoms [2], for several free-electron substrates, appropriate to simple metals. They also applied their techniques to adsorption on the simplest model of transition metals, the single-band, tight-binding model for a simple cubic crystal, studied by Einstein and Schrieffer [3]. LK’s elegant approach, however, requires several extremely restrictive conditions: substrate isotropy, weak adatom–substrate coupling, and poor matching of adatom and Fermi energies. This paper sketches a more general approach to the calculation of the asymptotic pair interaction which avoids all these restrictions [4,5]. For most physically reasonable choices of the model parameters, the general asymptotic expression is inadequate to describe the actual pair interaction energy at the separations at which the adatoms interact with significant strength, except perhaps at the coarsest order-of-magnitude level. Moreover, the asymptotic limit often leaves out much of the important physics, saying essentially that a single wavefunction (the highest occupied) dominates the substrate’s response [6].

LK’s method relies unnecessarily on a relatively weak adatom–substrate coupling parameter V , thereby excluding completely the strong-adsorption regime in which a surface molecule is formed [3,7]; it also requires the substrate Fermi energy E_F to be far from the characteristic adatom energy level E_0 , thereby excluding the energies relevant to covalent chemisorption. An asymptotic expression is generated for arbitrary substrate Fermi energy and V (but only in the high symmetry directions) by focusing on the propagator between sites of the unperturbed substrate surface. A table compares these results with exact results [3] and with the expression used implicitly by LK. The asymptotic expression adequately reproduces the exact behavior for large interadatom separations (R of several lattice spacings) but does not do well for smaller R . As expected, LK’s expression, which requires an isotropic Fermi surface, agrees well with the general asymptotic expression [only] near the bottom of the band. Near the band edge, the asymptotic expression becomes a *worse* approximation for the small- R behavior as E_F further approaches the edge, due to a breakdown of the asymptotic assumption. This regime is physically interesting (the interaction is always attractive) but of little practical consequence.

Capsulizing the needed formalism, one writes the interaction energy between an atom adsorbed above some site which can be called the origin, $\mathbf{0}$, and a second adatom at a site labeled $\mathbf{n} = (n_x, n_y)$ [where n_x and n_y are integers and the lattice constant is set to one so that [8] $R_n = |\underline{n}|$ as [2,3,9]

$$\Delta E_{\text{int}} = -\frac{2}{\pi} \int_{-\infty}^{E_F} \text{Im} \ln [1 - V^4 \bar{G}_{\text{aa}}^2(E) G_{\mathbf{0},\mathbf{n}}^2(E)] dE. \quad (1)$$

V is the Anderson model [10] adatom–substrate matrix element; the unit of this and all other energies is one-sixth the substrate bandwidth (i.e. $T = 1/2$). The energy zero is the band center. The renormalized diagonal Green's function for the adatom is

$$\bar{G}_{\text{aa}}(E) = G_{\text{aa}}(E) / [1 - V^2 G_{\text{aa}}(E) G_{\mathbf{0}\mathbf{0}}(E)] \rightarrow [E - E_0 - V^2 G_{\mathbf{0}\mathbf{0}}(E)]^{-1}, \quad (2)$$

where the final expression applies when the unperturbed atom is described by a single eigenvalue E_0 . Finally, the substrate propagator is $G_{\mathbf{0},\mathbf{n}}(E)$ is the sum over the square surface Brillouin zone of $\exp(i\mathbf{p} \cdot \mathbf{n})$ where \mathbf{p} is the two-dimensional crystal momentum, times

$$G(E, \mathbf{p}) = 2\{ [E - E(\mathbf{p})] + i[1 + (E - E(\mathbf{p}))^2]^{1/2} \}, \quad (3)$$

where $E(\mathbf{p})$ is the tight-binding eigenenergy $-\cos p_x - p_y$.

To obtain the asymptotic form of ΔE_{int} , one first expands the logarithm in (1), yielding

$$\Delta E_{\text{int}} \sim \frac{2}{\pi} \text{Im} \int_{-\infty}^{E_F} V^4 \bar{G}_{\text{aa}}^2 G_{\mathbf{0},\mathbf{n}}^2 dE. \quad (4)$$

Obviously the integrand of eq. (4) must be small to allow this expansion but this smallness can always be achieved via $G_{\mathbf{0},\mathbf{n}}$ for moderate R_n ; no weak- V ansatz is needed. LK's neglect of the V^2 term in eq. (2) eliminates the possibility of the bonding and antibonding resonances of a surface molecule and produces an unphysical divergence at $E_F = E_0$ [11]. Moreover, the energy range near E_0 is optimal for this model since the covalent bonding effects are strongest, and correspondingly the charge transfer is minimal, obviating the need for ad hoc self-consistency attempts [2].

The asymptotic form of $G_{\mathbf{0},\mathbf{n}}$ has been computed at *all* energies for the two symmetry directions $\langle 10 \rangle$ and $\langle 11 \rangle$ i.e. $n_y = 0$ and $n_y = n_x$, respectively. This form is dominated by the singularities in $G(E, \mathbf{p})$ at $E = E(\mathbf{p}) \pm 1$. For $|E| > 1$ (the outer thirds of the band), only one of these enters. To get $G_{\mathbf{0},\mathbf{n}}(E)$ an integral in the \hat{n} direction is first evaluated [4] using Lighthill's results for generalized functions [12]. The integral in the perpendicular direction is then carried out with stationary

phase arguments [13] yielding (for $|E| > 1$)

$$G_{0n}(E) \sim \begin{cases} -\frac{i}{\pi R_n^2} [(3 - |E|)(|E| - 1)]^{1/2} \\ \times \exp\{-iR_n \cos^{-1}[(2 - |E|) \operatorname{sgn} E]\}, & \hat{n} = \langle 10 \rangle; \\ -\frac{i}{\pi R_n^2} \left[\frac{(3 - |E|)(|E| + 1)}{(|E| - 1)} \right]^{1/2} \\ \times \exp\{-i\sqrt{2} R_n \cos^{-1}[\frac{1}{2}(1 - |E|) \operatorname{sgn} E]\}, & \hat{n} = \langle 11 \rangle; \end{cases} \quad (5)$$

where $\operatorname{sgn} E = E/|E|$. In the middle third of the band, both singularities in eq. (3) contribute. In the $\langle 10 \rangle$ direction, they cancel, indicating G_{0n} goes as $1/R_n^3$ at best; in the $\langle 11 \rangle$ direction (for $|E| < 1$), they added [4,5], giving two phase factors. Using the exponential oscillatory in R_n , eq. (4) is integrated by parts to give, for $E_F < -1$,

$$\Delta E_{\text{int}} \sim -\frac{V^4}{\pi R_n} (3 + E_F)^{1/2} f(\hat{n}) \operatorname{Re} [\bar{G}_{\text{aa}}^2(E_F) G_{0n}^2(E_F)] + O(R_n^{-7}), \quad (6)$$

where $f(\hat{n})$ is $(-1 - E_F)^{1/2}$ and $[(1 - E_F)/2]^{1/2}$ in the $\langle 10 \rangle$ and $\langle 11 \rangle$ directions, respectively [14].

To recover LK's result, consider the case $E = -3 + \epsilon$, $\epsilon \geq 0$, and set $k = (2\epsilon)^{1/2}$. In both directions eq. (5) reduces to

$$G_{0n}(E) \sim -i\pi^{-1} k R_n^{-2} \exp(-ikR_n), \quad (7)$$

and, since either f becomes just $\sqrt{2}$, eq. (6) reduces to LK's eq. (3.9) when \bar{G}_{aa} is replaced by G_{aa} [i.e. the V^2 term neglected in eq. (2)].

If eq. (6) is indeed an adequate weak- V approximation to eq. (1) for small R_n , then $G_{0n}(E_F)$ should be well approximated by its asymptotic form. Table 1 displays [5] both the exact substrate propagator and the asymptotic expressions given in eq. (5). (Only energies in the lower half band are listed since each part is symmetric or antisymmetric about the center.) $\operatorname{Re}\{-G_{0n}^2\}$ is also tabulated, since eq. (6) suggests ΔE_{int} is proportioned to this quantity (away from single-atom resonances, at least). The asymptotic expression does not do an adequate job of approximating the exact results, except for the largest values of R_n , where the interaction is too small to be of physical significance. Table 1 also lists $\operatorname{Re}\{-G_{0n}^2\}$ for the isotropic case [eq. (7)] used implicitly by LK; it closely resembles the general asymptotic result only near the band edge. Thus the inadequacy of the asymptotic approximation is not alleviated by taking the anisotropy fully into account.

Even near the bottom of the band, the scenario is more subtle than anticipated. (a) In LK's fig. 3, the curves suggested by the open circles representing "exact" energies are not damped cosinusoidal curves at all but just negative curves decaying with increasing R_n indicating that the interaction is *always* attractive. Accordingly, in LK's graph for $E_F = -5.6T$ ($\epsilon = 0.2$) the interaction energy for $R = 1$ (not plotted) is -2.8 in the units of their graph rather than something positive and large!

Table 1
 Surface Green's functions $G_{0,n}$ and the term asymptotically proportional to the indirect interaction energy: see text, especially eqs. (5)–(7), for details

n	Energy	$\text{Im } G_{0,n}$		$\text{Re } G_{0,n}$		$\text{Re } -G_{0,n}^{\text{ind}}$		Spher.
		Exact	Asym.	Exact	Asym.	Exact	Asym.	
(1,0)	-2.8	.025	-.153	-.136	-.115	-.0179	.0102	.0122
	-2.5	.092	-.138	-.161	-.239	-.0173	-.0380	-.0422
	-2.2	.169	-.062	-.151	-.306	.0059	-.0895	-.1327
	-1.9	.243	.032	-.108	-.315	.0475	-.0983	-.2195
	-1.6	.304	.117	-.034	-.267	.0911	-.0579	-.2778
	-1.3	.338	.159	.069	-.162	.1096	-.0010	-.2944
	-1.0	.325	.000	.200	.000	.0657	.0000	-.2649
	-.7	.244	.000	.300	.000	-.0304	.0000	-.1913
	-.4	.145	.000	.362	.000	-.1097	.0000	-.0796
	-.1	.037	.000	.390	.000	-.1505	.0000	.0612
(2,0)	-2.8	.022	-.013	-.046	-.046	-.0016	-.0019	-.0021
	-2.5	.065	.034	-.032	-.060	.0031	-.0024	-.0041
	-2.2	.088	.072	.009	-.031	.0077	.0042	.0034
	-1.9	.083	.078	.059	.016	.0034	.0058	.0131
	-1.6	.049	.050	.101	.053	-.0077	-.0004	.0163
	-1.3	-.004	.001	.117	.057	-.0136	-.0032	.0099
	-1.0	-.054	.000	.093	.000	-.0058	.0000	-.0037
	-.7	-.072	.000	.069	.000	.0004	.0000	-.0193
	-.4	-.091	.000	.044	.000	.0064	.0000	-.0314
	-.1	-.101	.000	.012	.000	.0102	.0000	-.0359
(4,0)	-2.8	.013	.010	-.002	-.006	.0002	.0001	.0001
	-2.5	.005	.009	.017	.015	-.0003	-.0001	-.0001
	-2.2	-.017	-.014	.013	.014	.0001	-.0000	-.0005
	-1.9	-.020	-.018	-.009	-.008	.0003	.0003	.0007
	-1.6	.000	.001	-.020	-.018	-.0004	-.0003	.0008
	-1.3	.015	.014	-.004	-.001	.0002	.0002	-.0008
	-1.0	-.001	.000	.006	.000	-.0000	.0000	-.0015
	-.7	-.003	.000	-.001	.000	.0000	.0000	-.0002
	-.4	.001	.000	-.005	.000	-.0000	.0000	.0017
	-.1	.006	.000	-.002	.000	.0000	.0000	.0021
(1,1)	-2.8	.024	-.064	-.071	-.081	-.0045	-.0025	-.0022
	-2.5	.082	-.021	-.073	-.171	.0015	-.0286	-.0241
	-2.2	.158	.065	-.038	-.223	.0177	-.0456	-.0367
	-1.9	.176	.178	.029	-.241	.0303	-.0262	-.0276
	-1.6	.185	.321	.119	-.224	.0201	.0530	.0015
	-1.3	.149	.549	.226	-.170	-.0292	.2721	.0415
	-1.0	.034	.000	.346	.000	-.1186	.0000	.0821
	-.7	-.171	-.286	.325	.606	-.0762	-.2856	.1138
	-.4	-.306	-.416	.210	.318	.0497	.0726	.1299
	-.1	-.367	-.474	.055	.078	.1320	.2183	.1269
(3,3)	-2.8	.011	.010	.000	-.005	.0001	.0001	.0001
	-2.5	.000	.007	.018	.018	-.0003	-.0003	-.0002
	-2.2	-.023	-.019	.008	.017	.0004	.0001	-.0001
	-1.9	-.022	-.031	-.021	-.011	.0001	.0009	.0007
	-1.6	.007	-.011	-.036	-.042	-.0013	-.0017	-.0001
	-1.3	.043	.040	-.015	-.050	.0016	-.0010	-.0011
	-1.0	.036	.000	.048	.000	-.0010	.0000	-.0004
	-.7	-.018	-.047	.028	.025	-.0004	.0016	.0011
	-.4	-.018	-.021	.005	.010	.0003	.0003	.0014
	-.1	-.012	-.001	-.000	-.005	.0001	-.0000	-.0000

(b) Eqs. (5) and (7) suggest that the density of states varies as $\epsilon^{1/2}$ near the band edge, as for the bulk. At a surface the density of states is narrowed and smoothed [15,16], producing a $\epsilon^{3/2}$ singularity at the edge.

(c) In table 1, the exact values of $\text{Im } G_{0,n}$, and hence $\text{Re } \{-G_{0,n}^2\}$ near the edge bear no resemblance to the asymptotic values for small R , even though LK showed that the pair interactions themselves should sometimes be comparable.

The source of all this peculiar behavior lies in the implicit assumption that $k_{\perp}R \gg 1$. For ϵ small, $\text{Im } G(E, \mathbf{p})$ becomes $2(2\epsilon - p^2)^{1/2}$, i.e., isotropic, and

$$\text{Im } G_{0,n}(E) = \pi^{-1}(2\epsilon)^{3/2} \int_0^1 J_0(st) t(1-t^2)^{1/2} dt, \quad (8)$$

where $t \equiv |p|/(2\epsilon)^{1/2}$ and $s \equiv R(2\epsilon)^{1/2} = kR$. For $s \gg 1$, the asymptotic form of the Bessel function can be used, producing a generalized function [12] expression and ultimately [4] the imaginary part of eq. (7). For $s < 1$, insertion of the small-argument expansion for J_0 yields a density of states going as $\epsilon^{3/2}$ and independent of n (to order $\epsilon^{5/2}R^2$) [5]. This result explains the surprising small- ϵ results in table 1. Away from resonances the integrand of eq. (4) now is proportional to $\text{Re } G_{0,n}(-3)$, with all R_n dependence coming through $\text{Re } G_{0,n}$ at the band edge [17]. Since $\text{Re } G(-3)$ is always negative [3], ΔE_{int} is also. For larger R_n , s becomes greater than one, and the analysis falters. Physically [18] in the small- s regime the adatoms couple to the lowest, bonding Bloch states of the substrate; since their wavelengths are long compared to R , the adatoms couple in phase. (For $\epsilon = 0.2$ and 0.5 , as in LK's fig. 3, k_{F} is 0.632 and 1.00, respectively, in inverse lattice constants.) Hence the pair interaction is uniformly attractive. Correspondingly, near the top of the band, the substrate orbitals are maximally out of phase. The sign of the interaction alternates with each lattice step of separation (going as $-(-1)^{n_x+n_y}$).

In conclusion, the R^{-5} -damped sinusoidal asymptotic form of $\Delta E_{\text{int}}(R)$ has again [3,15,19] been demonstrated for the outer thirds of the band; in the central third evidence suggests a decay going at least this fast (perhaps R^{-7} in the $\langle 10 \rangle$ direction) with a probably more complicated phase factor. This phase may be further complicated by broad adsorption resonances, near (in energy) which the perturbed adatom density of states ($\text{Im } \bar{G}_{\text{aa}}$) brings the imaginary part of the squared substrate propagator ($\text{Im}\{G_{0,n}^2\}$) into play. In practically all physically important situations on transition metals (as represented by a tight-binding model) the asymptotic expression does not give a good account of the indirect interaction. It will be correspondingly intriguing to check chemisorption onto a two-dimensional tight-binding model of surface states to find the minimum R for which LK's novel R^{-2} dependence for jellium is reproduced.

This work was supported in part by the University of Maryland Center for Materials Research (DMR76-82519). The computer time and facilities were supplied by the University of Maryland Computer Science Center and by Uni-Coll at the Univer-

sity of Pennsylvania. Part of this work was performed at the University of Pennsylvania, with support from NSF and ARPA. Helpful discussions there with Professors Michael Cohen, P.E. Bloomfield, J.R. Schrieffer, and Paul Soven are gratefully acknowledged.

Theodore L. EINSTEIN

*Department of Physics and Astronomy,
University of Maryland, University Park,
Maryland 20742, USA*

References

- [1] K.H. Lau and W. Kohn, *Surface Sci.* 75 (1978) 69.
- [2] For a recent review, see T.L. Einstein, *Theory of Interaction between Chemisorbed Atoms*, to be published in: *CRC Critical Rev. Solid State Sci.*; and in: *CRC Monotopic Series: Proc. Third Intern. Summer Institute in Surface Science 1977; Surface Science: Recent Progress and Perspectives.*
- [3] T.L. Einstein and J.R. Schrieffer, *Phys. Rev.* B7 (1973) 3629.
- [4] T.L. Einstein, Ph.D. thesis, University of Pennsylvania (1973), appendix.
- [5] This comment is a condensed version of University of Maryland Technical Report No. 78-056. This original report contains more extensive discussions, additional equations for $G_{0,n}$ and a larger table 1 which includes entries for $n = (3,0)$ and $(2,2)$ and an additional decimal place.
- [6] This viewpoint is embodied in the Woodward-Hoffmann symmetry rules of reaction chemistry.
R.B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.* 87 (1965) 395; 87 (1965) 2511;
R. Hoffmann and R.B. Woodward, *J. Am. Chem. Soc.* 87 (1965) 2046; 87 (1965) 4389.
As claimed in ref. [3], such rules are not reliable in describing the indirect interaction at small R ; they may be more useful when direct interactions are involved.
- [7] T.B. Grimley, in: *Molecular Processes on Solid Surfaces*, Eds. E. Drauglis, R.D. Gretz and R.J. Jaffee (McGraw-Hill, New York, 1969) 299;
D.M. Newns, *Phys. Rev.* 178 (1969) 1123.
- [8] It is important to keep in mind that R is not a continuous variable and the only translation which leaves ΔE_{int} invariant is through a lattice vector. (Cf. table II of ref. [3].)
- [9] E.g., G. Allan, *Ann. Phys. (Paris)* 5 (1970) 169;
W. Ho, S.L. Cunningham and W.H. Weinberg, *Surface Sci.* 54 (1976) 139; 62 (1977) 662;
N.R. Burke, *Surface Sci.* 58 (1976) 349.
- [10] P.W. Anderson, *Phys. Rev.* 124 (1961) 41;
also S. Alexander and P.W. Anderson, *Phys. Rev.* 133 (1964) A1594, with the direct interaction parameter set to zero.
- [11] In canonically transforming the Anderson Hamiltonian, a similar sort of resonance was noted and discussed by J.R. Schrieffer and P.A. Wolff, *Phys. Rev.* 149 (1966) 491.
- [12] M.J. Lighthill, *Introduction to Fourier Analysis and Generalized Functions* (Cambridge Univ. Press, Cambridge, 1958).
- [13] E.g. A. Erdélyi, *Asymptotic Expansions* (Dover, New York, 1956).
- [14] In arbitrary direction the analysis of the stationary phase points poses the added but surmountable difficulty. T.L. Einstein and L.D. Roelofs, unpublished.

- [15] D. Kalkstein and P. Soven, *Surface Sci.* 26 (1971) 85.
- [16] F. Cyrot-Lackmann and M.C. Desjonquères, *Surface Sci.* 40 (1973) 423;
F. Cyrot-Lackmann, M.C. Desjonquères and J.P. Gaspard, *J. Phys. C7* (1974) 925.
- [17] This dependence can be traced by explicit calculations or by using a moment expansion.
Cf. ref. [15] or T.L. Einstein, *Phys. Rev. B12* (1975) 1262.
- [18] The idea that some evidence of in-phase and maximally out-of-phase tight-binding states should exist near the band edges grew out of a stimulating conversation with Professor Frank Forstmann.
- [19] (a) T.B. Grimley, *Proc. Phys. Soc. (London)* 90 (1967) 751.
(b) T.B. Grimley, *Proc. Phys. Soc. (London)* 92 (1967) 776.
(c) T.B. Grimley, *J. Am. Chem. Soc.* 90 (1968) 3016.
(d) T.B. Grimley and S.M. Walker, *Surface Sci.* 14 (1969) 395.